

CLAIMS

1. A method of making a pigment composition, comprising the step of making a pigment selected from:

(i) a ferrocyanide derivative substituted with one or more cationic dye groups in the presence of a suspension of a zeolite pigment in an acidified solution; and

(ii) a derivative of a complex acid selected from the group consisting of: silicomolybdate, phosphomolybdate, phosphotungstate, phosphotungstomolybdate and mixtures thereof, substituted with one or more cationic dye groups in the presence of a suspension of a zeolite pigment in an acidified solution.

2. A method as claimed in claim 1, wherein the ferrocyanide derivative has the formula

(1):



wherein M is a transition metal selected from a copper, nickel or vanadium in a reduced state;

Z is a zeolite structure, preferably a zeolite pigment or calcined clay, more preferably an ultramarine base;

D is a cationic dye;

and p, q and r are integers from 1 to 3 wherein the total of $p + q + r = 4$.

3. A method as claimed in claim 1, wherein the complex acid derivative has the formula

(2):



wherein A is a complex acid;

Z and D are as defined in formula 1; and

q and r are integers from 1 to 3 wherein the total of $q+r = 4$ to 7.

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4. A method as claimed in any preceding claim, wherein the pigment is selected from ultramarine blue, ultramarine pink, ultramarine violet and ultramarine green and mixtures thereof.

5. A method as claimed in claim 4 wherein the zeolite pigment is ultramarine blue.

6. A method as claimed in any of claims 1, 2, 4 and 5, wherein the ferrocyanide derivative is functionalised with a dye selected from the following groups:

Diarylmethane type dyes such as Basic yellow 37

Azomethane type dyes such as Basic Yellow 65

Monoazo type dyes such as Basic orange 59

Xanthene type dyes including all Rhodamine dyes

Triarylmethane type dyes such as Victoria Blue

Coumarin type dyes such as Basic yellow 40

7. A method as claimed in any of claims 1, 2, 4, 5 and 6, wherein the ferrocyanide derivative is functionalised with a basic dye selected from:

basic blue 1, 3, 7, 9, 11, 26, 41, 54 and 162;

basic violet 1, 3, 10, 14, 16 and 53;

basic green 1 and 4;

basic orange 2 and 21;

basic brown 1 and 4;

basic red 7, 13, 14, 18, 22, 29, 46, and 51;

basic yellow 2, 5, 11, 13, 19, 24, 28, 29, 30, 37, 40 and 51;

basic red 1, 1:1, 7, 11, 13, 14, 18, 22, 29, 46, and 51; and mixtures thereof.

8. A method as claimed in claim 3, wherein the complex acid is selected from:

i) silicon, molybdenum, and / or tungsten (SMT) complexes; and

ii) phosphorus, molybdenum, and / or tungsten (PTM) complexes.

9. A method as claimed in claim 8, wherein the proportion of

$\text{SiO}_2 : \text{MO}_3$ is 1:(7-12); or the proportion of

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P₂O₅ : MO₃ is 1:(16-24);

wherein M represents the combined molecular total of molybdenum and tungsten.

10. A method as claimed in claim 3 wherein the complex acid derivative is functionalised with a dye selected from the following groups:

Diarylmethane type dyes such as Basic yellow 37

Azomethane type dyes such as Basic Yellow 65

Monoazo type dyes such as Basic orange 59

Xanthene type dyes including all Rhodamine dyes

Triarylmethane type dyes such as Victoria Blue

Coumarin type dyes such as Basic yellow 40

11. A method as claimed in claim 3, or any claim dependent on claim 3, wherein the complex acid derivative is functionalised with a basic dye selected from:

basic blue 1, 3, 7, 9, 11, 26, 41, 54 and 162;

basic violet 1, 3, 10, 14, 16 and 53;

basic green 1 and 4;

basic orange 2 and 21;

basic brown 1 and 4;

basic red 7, 13, 14, 18, 22, 29, 46, and 51;

basic yellow 2, 5, 11, 13, 19, 24, 28, 29, 30, 37, 40 and 51;

basic red 1, 1:1, 7, 11, 13, 14, 18, 22, 29, 46, and 51; and mixtures thereof.

12. A method as claimed in any preceding claim, further comprising an additional step of resination, wherein the resin is an alkali soluble abietic acid derivative.

13. A method as claimed in claim 12, wherein the resin is a pentaerythritol modified resin.

14. A method as claimed in any preceding claim, including the step of adding a surfactant.

15. A method as claimed in claim 14, wherein the surfactant is a non-ionic surfactant.

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16. A method as claimed in any preceding claim, wherein the quantity of zeolite is in the range of 5%-99%.

17. A method as claimed in claim 16 wherein the quantity of zeolite is in the range 70%-99%.

18. A method as claimed in any preceding claim, wherein the sum of the quantity of ferrocyanide, complex acid and dye is in the range of 1%-95%.

19. A method as claimed in claim 18, wherein the sum of the quantity of ferrocyanide, complex acid, metal and dye is in the range of 1%-30%.

20. A method as claimed in any preceding claim, wherein the amount of resin is in the range of 1%-20%.

21. A method as claimed in claim 20, wherein the amount of resin is in the range 1%-10%.

22. A method as claimed in any preceding claim wherein sulphamic acid is used to acidify the dye

23. A method as claimed in any of claims 1 -21 wherein a carboxylic acid is used to acidify the dye

24. A method as claimed in claim 23, wherein acetic acid is used to acidify the dye